Heterocyclic Chemistry
Prof. D. R. Mal
Department of Chemistry
Indian Institute of Technology, Kharagpur

Lecture - 14
Radicals in Heterocyclic Chemistry – II

Let me just repeat what I said few minutes ago, in the last class we talked about the heterocycles and the radical reactions right. Radical reactions is very famous now in organic chemistry, because of many reasons; one of the reason why radicals are popular, because they can survive in water solutions. And number 2, it does not promote, the radical reactions do not promote any elimination reactions will have plenty of examples today.

And then know what else? Third thing that it can be done in acidic conditions basic conditions; that means, they are not affected by changes in P H, then also they are not very susceptible to this other reaction conditions. Then radicals are generated normally by again 2 different kinds of genuine methods; one is the oxidative reagents, oxidizing reagents or the reducing agents. Like including lithium liquid ammonia, they are already reducing agent are say butyltin hydride then indium chloride, sodium borohydride all these, they all basically, the combination should be reducing agents, except of course hydrogen, hydrogen does not produce a radical reaction.

Then oxidizing agent could be manganese triacetate, let tetra acetate, phenyl hydrazine acetate, ceric ammonium nitrate all these are the oxidizing agents. Then we had looked at extensively, this menisci reactions; menisci reaction is going to very popular very recently and you have not got halt of the review, but I could recently one person has reboot the reactions, menisci reactions used in medicine chemistry.

So, you can think over it, that means it is primarily useful for medicine chemistry and if you recall in the last class we talked about extensively of the radical carbon radicals towards the paradigm moiety a paradigm derivatives, also agenda as an elastic example we also sort something else. That a complex molecule like quinine can be functionalize at particular position, of all possible positions only one particular position can be functionalize, that is two positions of the quinine moiety right.

Also you have noted one more important, which is otherwise impossible that, if you start with ethyl pyruvate, it can provide a functional group, which is not normally directly accessible, that is ester group. I mean if you can think of alternative you will find in alternative that by which one can that is directly deliver a carboxyl ester group to a nucleolus. So, the reactions in radical chemistry are very remarkable.

And today as I said before again, we will just see a duality of the reaction pattern, in the menisci reactions. Then also we will talk about this function alization of the 5 member hydro cellulose, how to do 5 member, they are not many options actually available. Although menisci is applicable to 5 membrane, but you have to have at least 1 or 2 nitrogen salute and but normally will see that under certain cases 5 member also can be functionalize provided, there is a limitation or there is I should say there is a guideline, under which condition 5 member are they in can be functionalized.

Just reverse, if you in menisci paradigm is the electrophile. So, the carbon radical is almost always nucleophilic almost not necessarily, but compare to paradigm yes carbonic profiles are necleophilic just change the situation. So, phi accessic heterocyclic means 5 members are necleophilic. So, if you have electrophilic kind of radical then obviously, functionalization would takes place, we have few examples.

Then will one and see and how to construct the heterocyclic ring systems, I mean there is no it is a very popular way of doing it, but that exclusively are used for non-aromatic heterocycles, understand what I am saying, it could be normally. But, we will look at some of the examples that will give some of the ideas and some there are impact radical chemistry can solve many, many unsolved problems.

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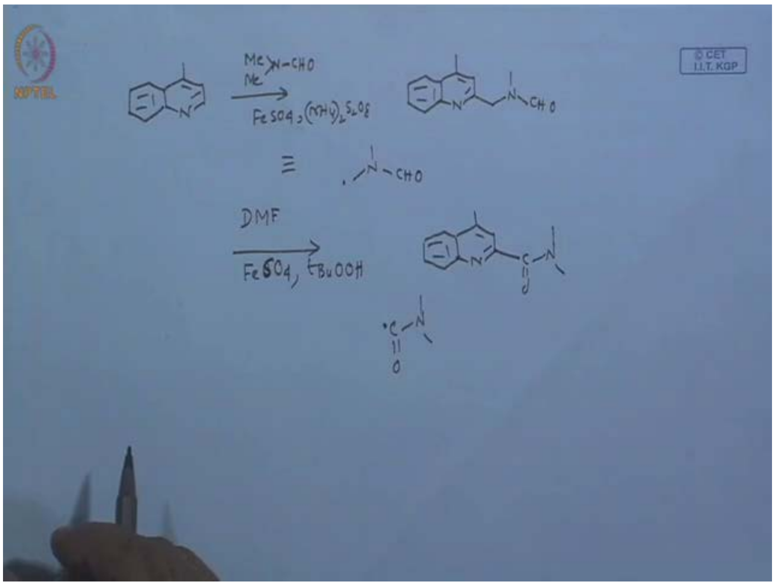

Let us look at this special menisci reactions, here is a case again the same volt quinoline and pore position is block. So, that it would not get, now without looking at if you can see red product, this is the carbon source and the reagent is thera sulfate ammonium perdisulfate. So, what would be expected just by looking at, you can see that ammonium perdisulfate is there, so it should peroxyl compound. So, it is likely that the radical would be generated from there peroxyl sulfate aionian radical, that would get another carbon radical.

Now, in this case, I can give you the answer, the answer is this, what would means this is equivalent to radical of this kind. So, again so basically manifester say redox potential as well as manifesters of the tertiary amine group effect, that mean this lone pairs of nitrogen stabilize the radical. And see the combination, you know on previous occasion we had only ammonium perdisulfate not in the therasulfate, therasulfate is normally used in the D M F.

Then therasulfate is normally used in combination with in hydrogen peroxide or the corresponding substitute, that is the soluble substitute, that is iso butyl hydroperoxide, under these conditions. So, what do you expect as I said, there is a duality reaction mode and what will find the just again, there is another possibility that, it can simply deliver the amide group that means radical, that was generated is acyl radical.

So, I mean either any prediction no absolutely no, at least one thing one can be done that the conditions can be modified to see whether that can be done this can be done that is the another thing. And let us say next item is the function alization of the 5 member heterocycle, one can think about let us say this is pre I think.

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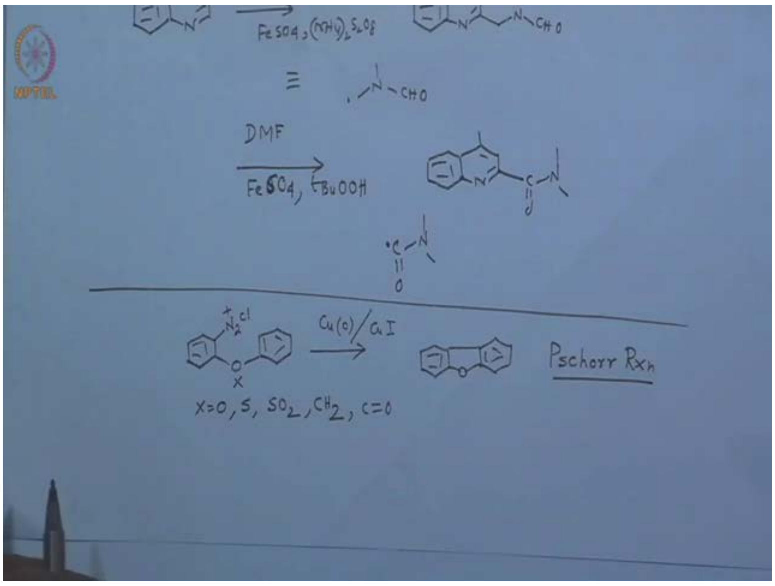

This is a reaction quite popular also in chemistry, suppose you have an oxygen of here, oxygen this and diphenyl ether then if you have a diazonium salt and treat this with copper 0 or copper 1 like cuprous iodide, you can expect to what is the reaction. Normally, the reaction that is the expected out of the diazonium salt and the copper salt is the basically, dimerization woon men coupling, but also we know, there if there is a reaction possible intra molecularly, that would be favor then favor to the intra intermolecular reaction and that is what happens.

And in this case, what do you get, you get the dibenzo furan that means, you can in the place of oxygen, one can think of that means, this is x. So, x could be oxygen, S could be sulfur, it could be S O 2, it could be even C H 2, it could be even carbonium, so such general reactions.

So, if it is general reaction then it should be named and what is the name, it is known as pschorr reaction p s c h o o sorry, r r reactions is pretty useful reaction. This reaction could be done in presidency college long above, when we are student one d n chatterjee present, d n chatterjee is to occur this reaction. And now very recently only very recently I think, I will give you the reference, if you are interested.

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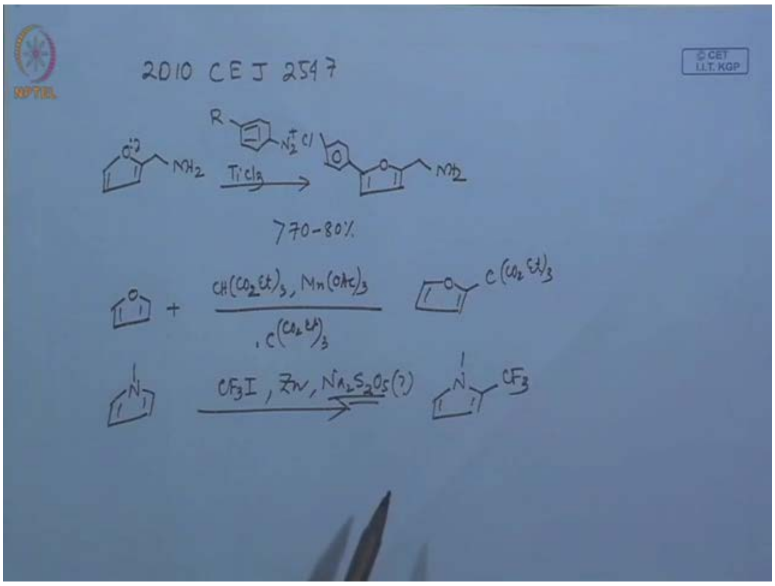

2010 I write in brief C E J chemistry european journal all of us know on the page number 2 5 4. So, what will do in this article, we again a very similar reaction has been the reported and what you will find, this is a substitute is furan containing amino group and the other reactant is diazonium salt and R often is in alkyl group then what. I will give you the n product is this amino N H 2 also this. So, what you find the yield is good more than 70 to 80 percent, but something is missing, what is missing, you have to generate the radical, so dizonium salt you have a radical.

And in previous occasion saw reactions, so we have seen copper 0 of copper, but then they are all heterogeneous reaction, so you have to have a homogeneous reactions. In fact, there is a reagent titanium trichloride many of you know this is a actually available in water solution. So, if you do, so the reaction actually generate radical and eventually adds to the now, you can guess on the position wise, see all of us know because of the a lone to are effect to the furan is nucleophile prominently at the 2 position or 5 position right.

So, 2 position or 5 position, so and provided furan act as a nucleophile that means, the in this case radical, that is being generated each electrophilic in nature. So, that is gives you the nice clear example, what does do you learn from this example, see basically what do you do write just reactions, what you have to extract out the useful information for it, what is other striking point about this particular reaction.

The amine group is protect unprotected so that means, amine is not at all effected by see in most other electrophilic reactions nucleophilic substitution reactions amines are always protected. What you means care you do not have to worry about the protection, we will see more example in radical reactions, similarly one more reaction let us say. Here you have triacid ester triester and then manganese acetate again an oxidize agent amine it the previous one was reducing agent and in this case it is oxidizing agent and the reactions the reaction would take place fine.

So, manganese trioxide triacetate it is an oxidizing agents, so it would actually generate the radical like this, so is a carbon radical. Now, you have to make a guess whether this carbon radical is electrophilic and nucleophilic, obviously, because you have 3 ester groups, so they are likely to be the electrophilic in nature and pleurisy nucleophilic and at the same time, so it should work at C 2, that means, the product could be this one.

And then n contras, if you take a let us say pyrrole moiety and this different the agent now, different the agent, what is there trifluoro methyl iodide and the other reagent is zinc and along with that actually, we have to question little bit in mine note it is given N a 2 S 2 O 5, I do not know what it is. So, I have to check with this N a 2 S 2 O 4 is sodium di thionite.

Students: ((Refer Time: 14:40))

H 2 h no, H 2 S O 5 is correct, acid that is an oxidizing agent, so together you cannot use it, so it has to be that is why I am telling that, may be there is a mistake, but any case for now, but it, but you just write down, that this reaction I have to check actually, forgot the source. But, as usual the reaction would take place and halides, halide on reduction gives the corresponding radical, that is almost always starting from the very early reactions called woods reaction, so ok.

And obviously, radical, but see mater of now, which one whether electrophilic or nucleophilic and in this case, here again 3 fluorine in the substrate. So, it is likely to be the electrophilic in nature and you can directly this sort of a kind of a field cursor, but in the radical mode. So, now we go to the next one.

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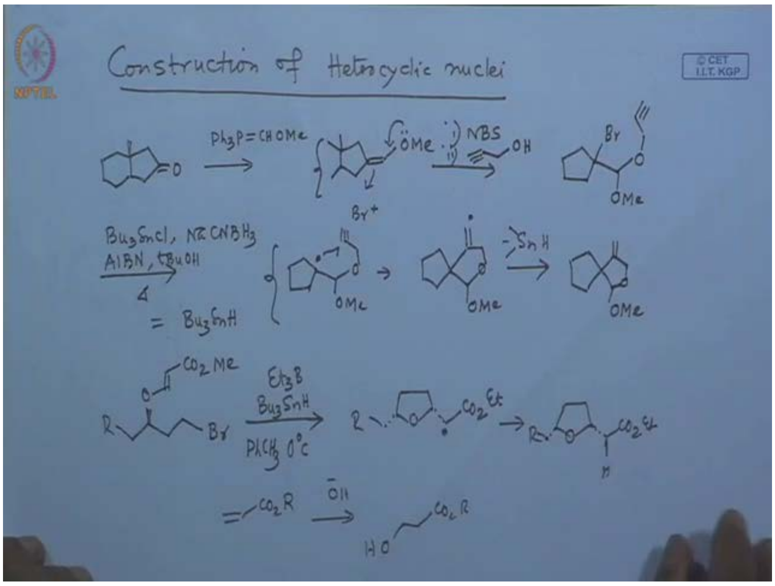

Construction of Heterocyclic nuclei

The next important topic actually is construction of heterocyclic nucleus right, heterocyclic nucleus by radical reactions, when I say so if you recall I said in most cases the reactions are used for non aromatic heterocycles. I will give you a quick sequence of reaction the 2 just example phi the radical reactions can be utilize for the construction of the heterocycles, the first few reactions should be for the oxygen heterocyles.

This one is I told you in this 4 year, this is a case of furan construction, the we will just ignore rest of the thing all of us know that, if you do a wittig reaction, wittig reactions with a methoxy methyl iodide, methoxy butyl reagent. And so the first thing that would take place is the wittig reaction then be formation of the double bond I think, I just write this second bracket. Then you do a small manipulation kind of thing, you react with N B S, N bromo succinimide and alcohol acetylenic alcohol, I will not tell you the name some of you know the common name.

Students: Propargylic alcohol

Propargylic alcohol.

So, what do you expect out of it, nothing to do it heterocyclic radical, but just to a small exercise of organic chemistry, so what do you suspect. The back bond remains as it is how is that the reaction takes place in the this double bond, so because of this lone pear actually, then the bromonium ion is capture, that means in have a bromine right. Then this alpha position becomes positive little charged and this portion remains O M E then what you will see, basically you will get a bromoether right bromoether.

Next is a very useful reaction, what do you do, you say butyltin chloride used it, then I will not write something, you have to tell me and then one more reagent, that is required A I B N and then tertiary butanol to solubelize all these things then you have to heat it. So, what is the missing reagent.

Students: ((Refer Time: 19:19))

Close close not correct, N a.

Students: Cyanoborohydride.

Cyanoborohydride, so now, cyanoborohydride is basically this combination is equivalent to tertiary butyl tin hydride, so sodium over hydride reduces the corresponding chloride and this gives A I B N generates the radical. So, that means, I mean then radical this clean radical has; obviously, it has an affinity towards all of us by now know, it has affinity towards tin as well as halogens, especially bromine and iodine.

So, one can write that this would generate a radical and then as usual, you have an intra molecular possibility. So, it will undergo intra molecular reaction and you will have a spirocyclic and as well as spirocyclic heterocyclic O M E and double bond and then you have a radical up here.

What next then access tin hydride access tin hydride hydride will be abstracted, so you will be getting a methylene this compound. So, I mean this is now, there are rest of thing actually in order for this synthesis of the target molecular whatever, but this is basically what do you see here, that this radical can be generated from an halogen compound and the corresponding tin hydride. And that can be added intra molecular to the triple bond and the reaction can be stopped there, provided you use access amount of this.

So, and then you do not require any kind of a group on this acetylenics, acetylenics normally electron unsaturated right. So, radicals the carbon radicals normally is nucleophilic that, nicely what with this acetal look at another example, similar example here, you have an alkyl side chain again is a bromo compound. Now, the oxygen is a separate place from bromine and then you have an system reaction condition is slightly different, I say triethyl borane and butyl tin hydride, when I write butyl tin hydride actually, it means n butyl tin hydride.

Then only 0 degree and solvent is toluene, so whenever you see triethyl actually, triethyl borane, it is equivalent to ethyl radical in the presence of that, you have to remember in the presence of oxygen.

Otherwise pretty stable, if it is inert ready protected from oxygen water triethyl borane is perfectly stable, but if you just inject little bit of oxygen, it may catch fire that pyrophilic. And the same time it produces a ethyl radical is one of I mean is not very popular, because it is difficult to handle I am sometime, so or otherwise it produce the ethyl radical that probably generates the tin radical from there.

And then what is the advantage comparison to the pervious example and what is the advantage, you can just guess.

Students: ((refer time: 23:37))

Ethylene generated that escapes the solution, that is the another point, important point is this one temperature, you can nicely quickly do it 0 degree. And so that tin radical generates the alkyl radical, the alkyl radical and now we can say what is the product, the product could be this is R, I have just revert it in writing, so the radical now would be this one, that means the radical now undergoes mikal kind of addition that mikal addition.

What next there all possibilities, whenever you have a radical whenever carbocation, you have all cancel possibilities, it can abstract proton it can eliminate something it can undergo the rearrangement all these possibilities are there. But, this is why the reactions stops, that is the beauty, what does it tell you, the reactions now stops at this position and so we will have these groups and this so does it tell you anything, about anything away.

So, you have an hydrogen now, abstracted here, so you get it again heterocycle saturated heterocycle, what is the advantage anything special you see, that is what you have to learn, when you read in the literature or the read a book say, we keep on giving examples one after the other, but there are lessons from one to the other, you have you see something new. In the from the first 1, you see lesson is separate mod of producing radical from the same kind of substrate then the bromide, but we see that the temperature can be lower down to the reducing, because of the.

And now as I saturated 1 and what else do you see, normally I will tell you just 1very important thing about this organic chemistry, if you try to let us say you have something like this and mechanistically, if you have O H minus what do you expect that these the michael addition would take place right. Michael addition would take place, that is not a verily routinely used reaction listen being I mean mechanistically, possible someone probably possible all these things, but in real life the heteroatom michael additions are very tough.

And if you are lucky, if you are not explective the reaction would take place something like this. In most cases unexpectedly takes place, but I mean, in fact, at least I cannot define under these circumstances hetero atom michael addition would takes place, this circumstances you do not its very irregular. So, that is number 1, so that means, it is sort of any you can say product that, you are getting is just like an inter molecular michael addition product kind of a thing.

What else, I have already said to begin with today when I say the advantages of the radical reactions, if you had a carbon and you would not expect a reverse of these michael addition that means, elimination would have taken place, addition elimination, you have learnt pento addition elimination reactions. But, this is a kind of a test, that the reaction is proceeding true radical reaction and that is that is what is happening and you saw chemistry wise this is also alpha, this is also alpha, that is the outcome of this thermodynamic product stability of the product.

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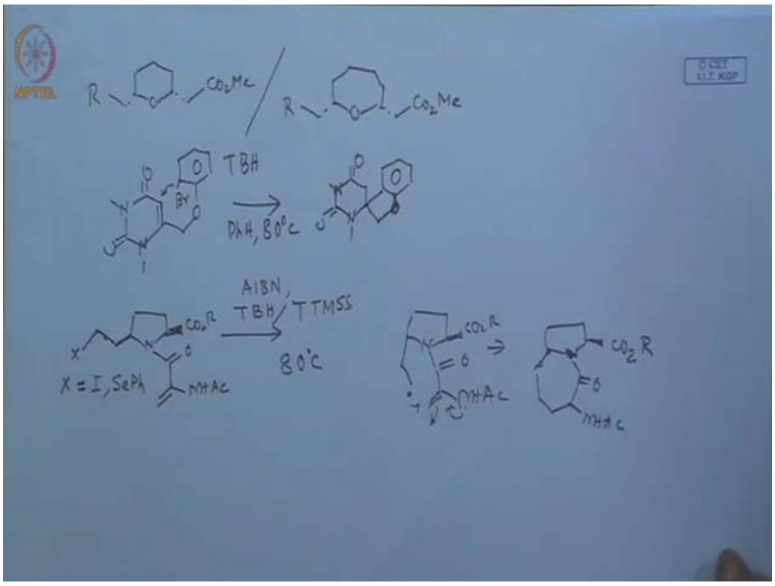

And likewise one can produce just similarly, just you increase the number of the carbon chain and you will be ending up with this product and also a like this that means, what I mean to say this reaction, this same reaction can be extended to preparation of the higher ring systems. I will let be give you one more example that means, still we are talking about the radical generation from the bromides and in this case, you say hetercycle here.

So, the starting molecule is in heterocycles with pyramided nucleus then carbon-carbon and then you have an oxygen and phenyl ring and you have a bromine lithier bromine atom here. Now, as usual tertiary butyl tin hydride, you can say is that is generated from butyl chloride etcetera and typical solvent is benzene or toluene and if it is benzene, the temperature is 80 degree centigrade.

So, what does it tell you, in this case a bromine sitting on the aromatic ring also can produce the phenyl radical, so that is it nothing else. So, previously it was S p 3 carbon atom, now it is S P 2 carbon atom, that can be also generated by and plenty of reactions have been studied under these conditions.

Once a radical is formed then you have to see an under there are all of us by now know, there are all kinds of reactions it can form the radical generated can form a 6 member as well as a 5 member. And normally, 5 X o is more favor, so what we will get this is the ruby inter molecular reaction would be taking place. So, you will have rest remains as it is and 5 member ring and these corresponding the benzene ring system, that is the typical one the yield is very good, it should be 5 member, it should be right.

So, its 5 member 1 2 3 4 5 membering systems, I will give you one of one more reaction very is quite similar, but the strikingly useful, if you here is an example, where you have side chain with x is x could be iodine or even selenium P H, that is phenyl selenyl and this nitrogen contains a double bond and another double bond with n h and a c. The reaction condition all again kind of that means, A I B N, it could be tertiary butyl tin hydride and the tertiary butyl tin hydride can also be substituted by any other kinds of hydride, any idea anybody knows, what are the other possible hydrides, there are hydrides right.

Hydrides means normally, we talked about metal hydrides, if you do not talk about the metal hydrides then we go to talk about boron hydrides, boron hydrides in also are classified sometime as the metal hydrides, what else then you want more hydride, one more kind of hydrides.

Students: ((Refer Time: 31:54))

Right sylvan hydrides, so actually, I did not get the name, but it appears to the there is a name in my note, this T T something like that, T T M S S, I think some sylvan, I have no idea, but the sylvan's are plenty in literature, they are commonly used. So, essentially basically this radical set, radical set and this temperature radical conditions then temperature is this, now let us say what do you expect, what do you expect, while iron is there hydride is there.

So, radical would be generated that means, the one that what one would expect this radical would generate sorry, radical would be generated, now you have this N H and A C. So, what next 7 member ring formation, so there is that means, a sort of a michael reactions when it although, you have amine deliver the lower pair in the reverse direction by this.

So, it is not a very good micro accepter, but yet the reaction would take place and the of this actually, in original compound, you have an ester group, you appear ester group and what we will find, you will find a bicyclic compound with a 7 member ring with a 7 member ring and then you have this N H A C and here, you have this ester group.

So, what is the conclusion from this one, that means, you do not have to have a very good 2 examples tells that, you do not have to have a very good michael accepters, but still the reaction can be done and then again this N H is not protected as a partially protected, that also to induce the cyclication. Let us look at one more very useful reagent, I do not know, there you know or not samarium iodide, you have heard of it right.

What, but what is the use actually, what is the use anybody knows any idea radical generation, that is carbon amine carbon amine radical. So, I mean you can what you can say what else or you can say metal transfer agent.

Students: Alcohol.

Not really that is the for.

Students: Disalolism

Yes I will take it good yes.

Students: Carbon-carbon bond formation.

That's true general, you have to be little more specific, what you said is correct carbon-carbon bond formation that is like what he said also is correct, that it can be used for desulphonation.

Students: ((Refer Time: 35:09))

Yes, it has some resembles with not mcmurry coupling means or you can say pinacol coupling, so it could be a substitute for the pinacol coupling. So, that means, it forms the carbon radical from a ketones, that is important not for the ester carbon radical like say pinacol rearrangement a pinacol formation, what is the metal.

Students: Magnesium.

Magnesium in inert solvent, not solvents etcetera, so there are not many substitute though or the other substitute let say initial if you do not have magnesium model would reduce for pinacol rearrangement, sodium I never heard.

Students: Sodium pinacol.

For pinacol for pinacol.

Students: ((Refer Time: 35:59))

May I have forgotten is to I do not know anybody support save him now, any case there are not many a substitute though, but one person try to develop a substitute for magnesium in pinacol, that was best on at the movement, I do not recall, that is low valent benedum salts. Espidarsion from California, that is hitrite and what is this samarium is a very useful 1, samarium is a useful then but how is useful, I do not know, but today, we will be seeing, that it can produce the carbon radical. Carbon radicals are from that means, oxy carbon radical from ketone.

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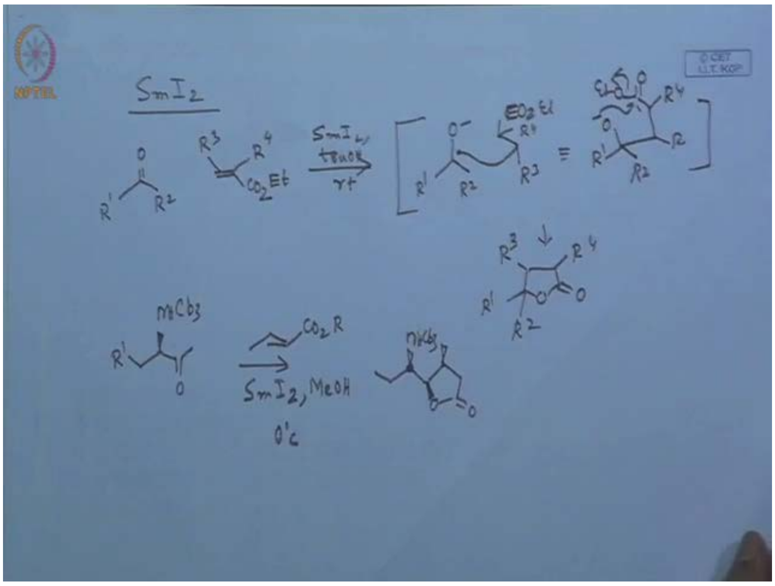

That means, if you start with a ketone and this oxygen up here and then let us say, you have an alpha beta unsaturated ester, you get a you get an inter molecular reaction, that the condition the condition is very simple samarium iodide and then tertiary butyl alcohol and room temperature, you do not have to heat and do anything, just a room temperature. So, what do you expect what, I said that it first forms a radical that means, anion here and the radical here means R 1 and R 2.

Now, we have a substrate, which a michael accepter and most of one now said is carbon radicals are nucleophilic in nature, so after the reaction is what will find, if you write this ester in this of a fashion e are normally, I write, I think, I should write this, ester group here then R 4 and this is R 3 that means, it goes to the this 1, so that means, alpha beta position.

So, that means, it is equivalent to what you can say R 1 R 2 and here you have R 3 then this R 4 and you have ester here, and you have an oxygen minus so anion radical. And obviously, and all of us know, you have 5 member whenever that proceeds a very smoothly. And so eventually what you get is again is of furanone now, so eventually what you get is the I mean furanone, you can call it as a lactone and you can call it also you can call it as a heterocycle.

So, you have all kinds of this is a nice reaction intermolecular reactions, now I mean the same reaction is let us say now you just change this, you have definite subset of here. What we will have now N H c b z carbon dioxy carbonic benzyloxy and this is R 1 then again, you have here michael accepter and what do you expect, now the state way write the product without looking at the reaction mechanism just a simple then the methyl group of here, this is a methyl group and this is a N H and c b z.

Then that means, you have a what you see here, so why did I chose this example this has also this has also a why did I chose this example any idea, this is a this reaction also is carried out with samarium iodide, the reaging condition is methanol samarium iodide and 0 degree that means, that the previously that the room temperature is 0 degree.

And what is the remarkable about this reaction remarkable, it is remarkable in many respects number 1 that, you get 3 different chiral centers fixed under the influence of one paral center you can get the 3 different paral centers, you are forming a new carbon bond. What else, that you what is important in see, in case of a carbonic compound having an a alpha chiral center many of an will see the racemisation of the stereo mutation takes place.

So, what is in under the radical reactions elimination does not take place racemisation does not take place and the outer position, so these are the advantages with samarium iodide radical kind of reactions. Let me give you one more many of you know the polyethers are very useful biological molecules biological molecules, I will just give you only one example may be that will tell.

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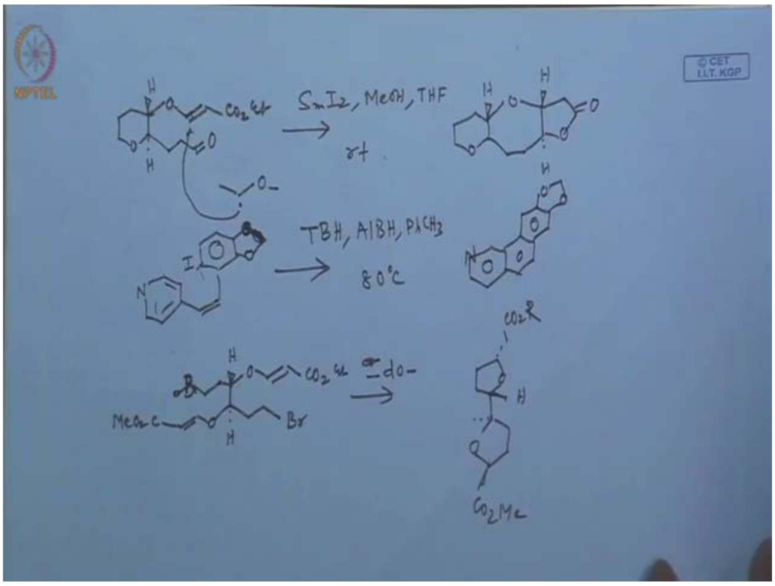

You know how useful is samarium iodide or if you think about alternative methods, you will not find alternative method for these here is a tetrahydro pyran case, oxygen of here. Then you have ester and I will just give, you there are plenty of examples in my note, but I will just, so give you one here and once again samarium iodide what else you require methanol and the reaction methanol T H F and the reaction condition is room temperature.

I think all of so be able to write this structure right, what is the structure, this let me in this case here it is also trans, so that means, this ring junction street chemistry remains unaltered. And mentally, you have work on that the samarium iodide actually reacts with only ketone compounds; that means, it will it will form an oxygen negative and carbon radical, so anyon radical is produced. Once anyon radical is produced, either the undergo coupling, self coupling or intramolecular cyclization that is it.

That means, this radical would attack the intermolecular version and eventually what you will find, a 7 member ring right. That means, 1 2 3 4 5 6 7 and this stereo chemistry as usual, especially when you have the polyethers, you will find all these hydrogens in across the heteroatoms are normally says, because of their anomeric effects. This hydrogen and here, you have then the lactonization takes place because you have an alkoxy this alkoxy alkoxy expellls the ethoxy groups, so you get the lactonization done.

And so what else, what is other thing, that you can think of again, there is no elimination taking place say when I takes place had it been an carbon ion, you would expect this oxygen substituent. So, in that case, you would not have obtained this metal ring, so that means, what you can that means, you can nicely construct the polyether like, if you begin with other ethers on the left hand side etcetera, you can generate polyethers fine. So, is a basically, good example of the samarium iodide case.

And now, we move on to just say again different kind of the examples that is it and but the mode is very similar, I think this is what you have to see that, this is this methylenedioxy bridge here, methylenedioxy this is oxygen C H 2 oxygen and tertiary butyl tin hydride T B H, I will write A I B N and then toluene. This is commonly you sets of reagents and conditions and then temperature 8 degree though toluene, it can go up to 110 and what is the product.

So, now, we have to sufficient of experience to predict the product, so what is could be the product, you start from the reagent whenever you have to predict a product, you start from the reagent. So, T P H is typically generates the radical, either at the S P 3 or S P 2, so it will this then what then immediately, you should think of the intermolecular reaction, so it can form the 3 member right, double bond is not that electrophilic in nature.

But, instead you have radical here, there is a possibility that, it can undergo reaction showing the heterocycles that is it and here sort of an minisci reaction carbon radical, but though minisci reactions, we recall that involve normally, the S P 3 carbon atom. And eventually, so this gives you rise to a few heterocyclic ring system and you have all these that means, so in that is way that is what you have to be little careful about or you can I mean, that these heterocyclic systems also could be an electron sink, means it can accept electron.

And so there are other examples may be, let be I think, I will skip some of the examples may be and there are most of the examples are typical examples of this tin hydride etcetera etcetera, I think I will skip some of them may be, I will give this one is quite little interesting. In the sense that, you get 2 heterocycles, if you have properly design substrate oxygen of here, again these beta oxy acrylates and then you have a side chain with bromine and you have one more unit of the butyl oxy esters.

Then hydrogen and you have 1 2, so you have this 1 2, so this is bromine sorry, so bromine, now I think again I think, I will write this just do means on the whatever written on the top is this, so what is the product any idea. What is the product, I mean this is a I mean both are I mean all the side chains are this is same as this one this is.

Students: By cyclic ether.

By cyclic ether that means, a 6 member by cyclic ether. So, the means at least, we know that S P the radical would be forming and intramolecular reaction that is a typical actually, there are reaction of this kind. And only thing that, you have to mean now little careful is that the reaction gives a so what is the conclusion, so you have competition now, you have competition first 5 and six 5 and 6 and often 5 is more fissile. So, I think, we have talked in a about enough of this thing, I will give you one more example where, very similar that radical being generated from yes.

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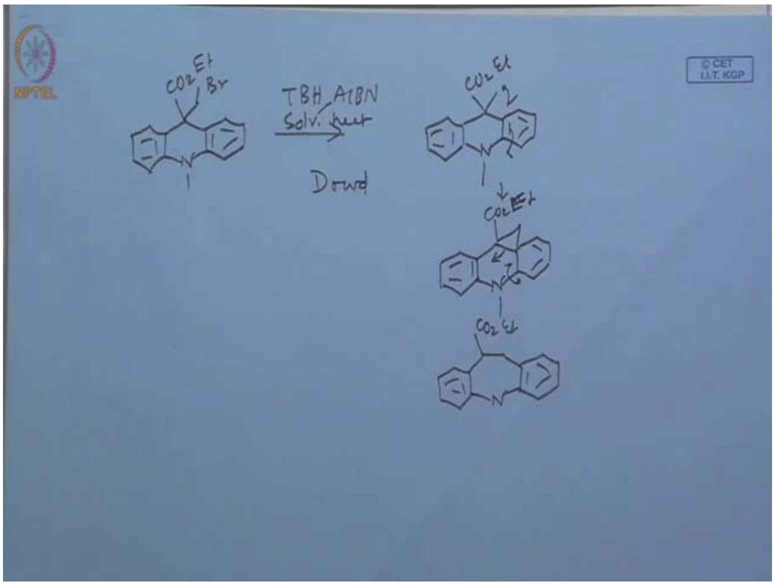

Let us see I think I have many examples, this is a case many of you would not know, because this is a specialized case, here you have when heterocycle and then you have ester group here. And then now, C H 2 and bromine and the reaction said again T B H typical, this a I B N and the solvent and then heat, so what do you expect, if you know that dowd ring expansion then dowd ring expansions.

For dowd, we has unfortunately died at early age, because in pittsburgh and he had nice way of ring expansion, if you have a kito compound normally, cyclohexanone how do you go to the cycloheptanone, in the honest level most of you write diazomethane right. Diazomethane, but those reactions are very lowery reaction actually, the low yielding reactions etcetera, but he developed nice protocol for ring expansions this is the that is a something this like.

So, what do you see, here it first if you step wise proceeds, then what will find the reactions are pretty easy to take low, so you have now radical here. So, what next the internal price x, hows that in term co reactions, now you see this is a combination of very interesting there, this is not a pyridine though the middle ring is not a pyridine ring, but it has some advantage, you get a radical alpha to the nitrogen. What does it mean, you have an extra stability although rehabilitation taking place, but the radical that is being generated, it has some it has gains some due to these lone pair effect.

And So, you will have the ester group here and you have triple bond what next you would goes back, then you get the starting material, what is the starting material, so re aromatization and the ring expansion takes place that means, the middle rings, now becomes a 7 member ring. So, that means, I mean you can logically approach and eventually, you can get to the right answer. And I have many more examples many more example, I will skip them, I think very quickly, I will go to the last example.

In the last year, we talked about a reaction right. this the we talked about the radical reactions of cyclopropyl methyl radical, in the context of establishing the radical reactions.

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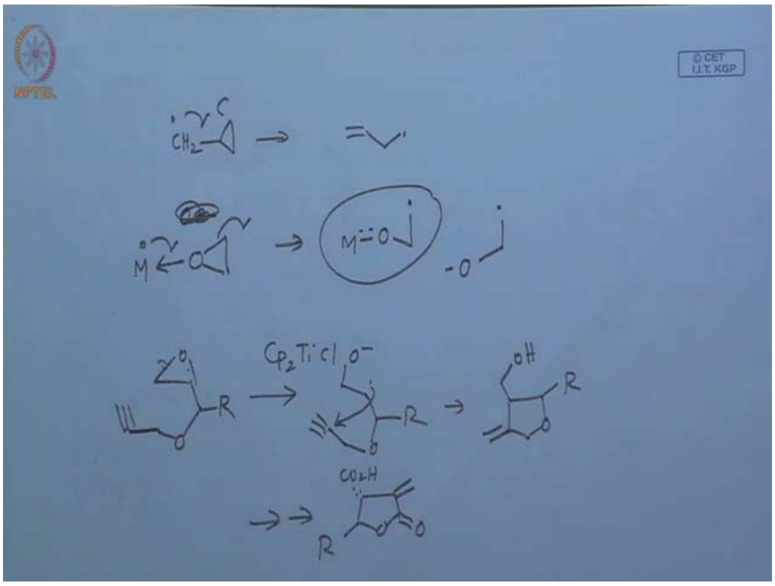

What is this it is a radical probe anybody knows, what is the meaning of the radial probe, I means, if you are want to distinct with that reactions, whether it is carbonium ion reactions, radical reaction or carbon ion reactions, one of these way is to use this sort of radical, it opens then the reaction must be consider a radical reactions. If the is opened that means, the adjust an automobile radical.

Now, if you substitute this with a let us say metal; that means, oxygen of here and is a cyclopropane right. Now if you coordinate with a metal and metal has a additional electron pair, then there is a chance that it would open up and it will give rise to something like this. So, what is it, so that means, you have to have a, which is reducing agent, what you get out of this and how do you call it, this is an radical having an oxygen minus you can say, if you recall the summary am I did produce, radical 1 to the carbon having the oxygen, now it is what is that the beta position.

And this sort of reaction is done and in cultivation of science almost regularly by and it was invented by one annual scientist Rajan Babu state have you heard of him, Rajan Babu and some other person, when he was in an industry, not in I have a state.

And reaction just I will give you just only one example, this is nice way reaction though nice reaction, if you let us say begin with an epoxide that means, what is the requirement you have to have a epoxide and let us say r oxygen propyl zyl group, propyl zyl group oxygen and this. So, I am the metal here, C P 2 titanium chloride etcetera, so then say reducing metal.

So, gives you the that means, now you have to think here, you have radical opening on this side you have radical opening on this side all of us know radical like carbonium ion radical secondary carbon radical is more stable. So, the radical that would be generated is and radical of here. And he has publish plenty of papers in this thing, since we do not have time I will this.

And so what else, that set I means what will get 1 2 3 4 5, so will have a again a furan ring, furan ring are and then this is now double bond and you have O H group here. So, you have an O H functionalize furan and all the carbons are almost like functionalize, this is having oxygen, this is having S P 2 carbon, this is also C H 2 having say functional group. And this compound eventually, converted into natural products call is a natural products, something like methyl lactone or something and is a natural products this and it has a R group of here. So, in multi step they have been a produce this.

So, this is another E V way producing radical and so what else, I think we did not give you examples time is now, then one more example, I think you have to take note of that is a phenyliodonium diacetate. So, phenyliodonium diacetate is also becoming a very popular radical generated and often it is use to produce radical from the benzene requisitions fine.